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(54) Title: PEROXYGEN CLEANING COMPOSITION

(57) Abstract

An aqueous composition, comprising phosphoric acid and/or sulphamic acid, a compound which generates a peroxygen species in acidic aqueous environments and a surfactant, may advantageously be used in the brewing industry for cleaning process vessels operating under carbon dioxide atmospheres and in the dairy industry for reducing the quantities of alkaline effluent which needs to be neutralised prior to discharge to the public services.

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PEROXYGEN CLEANING COMPOSITION

This invention is concerned with compositions suitable for use as cleaners. More particularly, this invention concerns novel acidic cleaners comprising phosphoric acid and/or sulphamic acid, suitable for use in the dairy and brewing industries.

DD 117352 (Kabus) describes a process for cleaning reverse osmosis and ultrafiltration membranes with a solution containing phosphoric acid and a per acid.

SE-A-7608459-9 describes that phosphoric acids having the capability of binding divalent metal cations can stabilize peracetic acid.

WO 91/07375 (Eka Nobel) relates to a composition containing peracetic acid, hydrogen peroxide, mineral acid and water. In order to improve the stability of the peracetic acid, the composition also contains dipicolinic acid and at least one phosphoric acid having the capability of binding divalent metal cations into a complex.

Traditionally, alkaline pH cleaning systems have been used in cleaning the equipment used in the brewing and dairy industries. However, a number of problems arise using such systems. In hard water areas, limescale deposits build up upon the metal surfaces, which eventually can lead to clogging of pipes and valves. In brewing systems, a high CO_2 level is present. This effects the efficacy of alkaline cleaners as carbonates build up. A more suitable cleaning composition is required.

In accordance with the present invention there is provided an acidic aqueous composition comprising:

1) an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof;

2) a compound which generates a peroxygen species in acidic aqueous environments; and

3) a wetting agent stable in an acid/peroxygen aqueous environment.

Preferably, the aqueous composition comprises at least about 10% by weight, more preferably from about 10% to about 50% by weight, and most preferably from about 25% to 35% by weight, of component 1).

The acid preferably comprises phosphoric acid alone, rather than sulphamic acid alone or in combination with phosphoric acid.

The peroxygen species in the aqueous composition are preferably generated by using component 2) in preferably at least about 1.5% by weight, more preferably at least about 1.75% to about 5% by weight, most preferably from about 2% to about 4% by weight, of the total composition on formation.

Any compounds which generate a peroxygen species in acidic aqueous environments may be used in the composition of the present invention. Preferred such compounds include hydrogen peroxide, peracetic acid and potassium permonosulphate. The compounds may be used individually or in combination, one peroxygen generator mixed with one or more other peroxygen generators, e.g. hydrogen peroxide mixed with peracetic acid. It will also be understood that a mix of peroxygen generator and acetic acid will

provide the peracetic acid species.

The aqueous composition will also comprise a wetting agent 3), i.e. a surfactant, preferably a low foaming nonionic surfactant, which is compatible with acidic/peroxygen aqueous environments and which may be used in an amount of from about 0.1% to about 10% by weight of the composition, preferably from 0.2-2.0%.

The aqueous composition may also comprise a carboxylic acid, preferably a C_1-C_6 carboxylic acid such as acetic acid, which is preferably added to the composition in an amount of from about 2% to about 20%, more preferably from about 5% to 10%, by weight of the composition.

The aqueous composition may comprise one or more other components which are typically used in industrial cleaning compositions. For example, the aqueous composition may comprise a sequestrant which is compatible with acidic/peroxygen aqueous environments, e.g. a phosphonate sequestrant such as Dequest 2010 available from Monsanto, and which may be used in an amount of from about 2% to about 15% by weight of the composition.

The aqueous composition may also comprise a suspension/dispersion aid which is compatible with acidic/peroxygen aqueous environments and which may be used in an amount of from about 2% to 15% by weight of the composition.

The composition according to the present invention may be used as a detergent and/or disinfectant. It is particularly preferred for use in cleaning in the brewing and dairy industries, and is also useful for the cleaning

of beerlines in pubs and clubs.

It has been found that acidic cleaning compositions according to the present invention provide efficient cleaning whilst not suffering from the problems described above. The compositions are particularly effective in microbiological cleaning. Without wishing to be bound by theory, it is thought that the presence of surfactants increases microbiological efficacy due to surface effects. The surfactant should preferably be chosen in order that residues do not affect the head formed in beer, and should also be low-foaming. Furthermore, the peroxygen component of the formulation according to the present invention contributes to cleaning by acting as an oxidising agent and by generating microscopic bubbles of oxygen which contribute to the physical aspect of cleaning.

In the dairy industry, the compositions are advantageously employed to substantially reduce the quantities of alkaline effluent which needs to be neutralised prior to discharge to the public services.

The cleaning compositions according to the present invention will also be more environmentally acceptable than chlorinated alkaline cleaners of the art.

Accordingly, the present invention further relates to a process for cleaning a microbiologically contaminated environment which comprises applying to said environment a cleaning agent comprising 1) an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof; 2) a compound which generates a peroxygen species in acidic aqueous environments; and 3) a wetting agent stable in an acid/peroxygen aqueous environment.

According to a further aspect, the present invention relates to the use of a composition comprising 1) an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof; 2) a compound which generates a peroxygen species in acidic aqueous environments; and 3) a wetting agent stable in an acid/peroxygen aqueous environment, in the reduction of microbiological activity in a microbiologically contaminated environment.

One embodiment of the present invention was made by the following process:
15g of phosphoric acid (85%) was added, with stirring, to 22.6g of demineralised water in a vessel. To this solution there was added, with stirring, 5g of Dequest 2010 sequestrant, 0.1g of dipicolinic acid (10% sol.), 1g nonionic surfactant and 3g of glacial acetic acid. The composition was stirred for 15 minutes to ensure a homogenous composition and then 4.3g of hydrogen peroxide (35%) was added dropwise over a period of 5 minutes. The resulting product was a clear homogeneous composition.

The invention will now be described in further detail.

The following composition (A) was prepared (all amounts are in wt%):

Phosphoric acid	27%
Peracetic acid	1%
Hydrogen peroxide	3%
Acetic acid	6.7%
Nonionic surfactant [1]	0.5%
Suspension aid [2]	0.5%
Dipicolinic acid	0.2%
Demineralised water	61.1%

[1] Ethylene CD 919 from Harcross Chemicals
[2] Dequest 2010 from Monsanto

The composition was compared for microbiological cleaning efficacy with a commercially available beerline and brewing cleaning product (B), which is a caustic/hypochlorite system.

All microbiological tests were carried out using a standardised suspension test. The biocidal activity of the exemplified product was evaluated against a suspension of the bacterium Lactobacillus brevis at an initial inoculum concentration of 1-3 x 10^7 cfu ml^{-1} (colliform units per millilitre) and compared to Savol against suspensions of the yeasts Saccharomyces diastaticus, Candida lambica and Candida pelliculosa, all at initial inoculum concentrations of 1-3 x 10^6 cfu ml^{-1}.

The tests were carried out in the presence of local tap water only (110-120 mgl^{-1} $CaCO_3$) to represent clean conditions and also in the presence of 4 gl^{-1} yeast extract in local tap water to represent soiled conditions.

The formulation of the invention was evaluated at concentrations of 0.5%, 1.0% and 2.0% under both sets of conditions. Savol was evaluated according to recommended concentrations, i.e. 0.5% under clean conditions and 1.0% under soiled conditions.

Contact times of 5,15 and 30 minutes were used.

The results from the experiments have been calculated as logarithmic reduction factors (LRF) and are collected in the accompanying tables. For high standard disinfection a LRF of >5 against the bacterium and LRF >4 against the yeasts are required.

The exemplified composition according to the present invention should preferably be used at a concentration of at least 1.0 wt% to be effective against all four microorganisms. The formulation may be adjusted to preferably contain 2.0 wt% peracetic acid.

The experimental results show that the formulation according to the invention is as effective as the commercially available product in microbiologically contaminated environments, but will not have the problems associated with an alkaline/chlorine environment. It has the additional advantage in that its action is not reduced by the presence of organic soils. The formulation can be used to both remove soil and reduce or remove microbiological contaminants.

TABLE 1

Lactobacillus brevis

	CLEAN LRF			SOILED LRF		
	5mins	15mins	30mins	5mins	15mins	30mins
0.5% A	5.6	5.6	5.9	●●●	●●●	5.6
1.0% A	5.8	5.8	5.9	5.3	5.4	5.5
2.0% A	6.0	+++	+++	5.5	6.0	6.0
0.5% B						
1.0% B						

●●● = LRF < 3

+++ = LRF > 6

TABLE 2

Saccharomyces diastaticus

	CLEAN LRF			SOILED LRF		
	5mins	15mins	30mins	5mins	15mins	30mins
0.5% A	●●●	●●●	2.6	●●●	●●●	●●●
1.0% A	3.2	5.0	+++	2.4	3.5	4.6
2.0% A	+++	+++	+++	+++	+++	+++
0.5% B	3.5	+++	+++			
1.0% B				●●●	●●●	●●●

●●● = LRF < 2

+++ = LRF > 5

TABLE 3

Candida lambica

	CLEAN LRF			SOILED LRF		
	5mins	15mins	30mins	5mins	15mins	30mins
0.5% A	3.4	4.8	5.0	●●●	●●●	●●●
1.0% A	4.9	5.0	+++	4.4	4.8	5.0
2.0% A	+++	+++	+++	+++	+++	+++
0.5% B	2.5	+++	+++			
1.0% B				●●●	●●●	2.9

●●● = LRF < 2

+++ = LRF > 5

TABLE 4

Candida pelliculosa

	CLEAN LRF			SOILED LRF		
	5mins	15mins	30mins	5mins	15mins	30mins
0.5% A	●●●	●●●	2.4	●●●	●●●	●●●
1.0% A	2.3	5.0	+++	●●●	2.3	3.4
2.0% A	4.0	+++	+++	3.0	+++	+++
0.5% B	4.3	+++	+++			
1.0% B				●●●	●●●	2.7

●●● = LRF < 2

+++ = LRF > 5

CLAIMS

1. An acid aqueous composition comprising 1) an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof; 2) one or more compound(s) which generate a peroxygen species in acidic aqueous environments; and 3) a wetting agent stable in an acid/peroxygen aqueous environment.

2. A composition as claimed in Claim 1 comprising from 10-50 wt% of an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof.

3. A composition as claimed in Claim 1 comprising from 25-35 wt% of an acid selected from phosphoric acid and sulphamic acid, or mixtures thereof.

4. A composition as claimed in any one of Claims 1 to 3 comprising from 2-4 wt% of peroxygen species.

5. A composition as claimed in any one of Claims 1 to 4 comprising from 0.1 to 10 wt% of surfactant.

6. A composition as claimed in any one of Claims 1 to 5 wherein the acid is a phosphoric acid.

7. A process for cleaning a microbiologically contaminated environment which comprises applying to said environment a cleaning agent as defined in any one of Claims 1 to 5, and allowing contact for sufficient time to reduce the microbiological activity present in said environment.

8. The use of a composition as defined in any one of Claims 1 to 5 in the reduction of microbiological activity in a microbiologically contaminated environment.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 93/00995

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C11D3/39; C11D7/08

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C11D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	DE,B,2 654 164 (SCHULKE & MAYR GMBH) 22 December 1977 see column 5, line 3 - column 6, line 18; claims	1,4,6-8
X	EP,A,0 013 886 (S.C.JOHNSON & SON, INC.) 6 August 1980 see page 6, line 25 - page 7, line 4; claims 1,9,10	1,2,4-6
X	DE,B,1 198 800 (HENKEL KGAA.) 19 August 1965 see column 3, line 15 - line 24; claims 1-6	1,4,5

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° Special categories of cited documents :[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
15 SEPTEMBER 1993	27.09.93
International Searching Authority	**Signature of Authorized Officer**
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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P,X	EP,A,0 517 996 (THE PROCTER & GAMBLE CO.) 16 December 1992 see page 3, line 39 - line 42; claims 1-6,8	1,4-6

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